Claims

1. (currently amended) A process for the preparation of acylphosphanes of formula I

$$R_{1} = \begin{bmatrix} \begin{bmatrix} R_{3} \end{bmatrix}_{2-m} & O \\ C - R_{2} \end{bmatrix}_{m}$$

(I), wherein

n and m are each independently of the other 1 or 2;

R_1 , if n = 1, is

 C_1 - C_{18} alkyl, C_2 - C_{18} alkyl which is interrupted by one or several non-successive O atoms, [[;]] phenyl- C_1 - C_4 alkyl, C_2 - C_8 alkenyl, phenyl, naphthyl, biphenyl, C_5 - C_{12} cycloalkyl or a 5- or 6-membered O-, S- or N-containing heterocyclic ring, the radicals phenyl, naphthyl, biphenyl, C_5 - C_{12} cycloalkyl or the 5- or 6-membered O-, S- or N-containing heterocyclic ring being unsubstituted or substituted by one to five halogen, C_1 - C_8 alkyl, C_1 - C_8 alkylthio, C_1 - C_8 alkoxy and/or -N(R_8)₂;

R_1 , if n = 2, is

 C_1 - C_{18} alkylene, C_2 - C_{18} alkylene which is interrupted by one or several non-successive O atoms; or R_1 is C_1 - C_6 alkylene which is substituted by C_1 - C_4 alkoxy, phenyl, C_1 - C_4 alkylphenyl, phenyl- C_1 - C_4 alkyl or C_1 - C_6 alkoxyphenyl; or R_1 is phenylene or xylylene, which radicals are unsubstituted or substituted by

-CH₂-C \equiv C-CH₂-one to three C₁-C₄alkyl and/or C₁-C₄alkoxy, or R₁ is a -CH₂CH=CHCH₂-,

group;

R₂ is C₁-C₁₈alkyl, C₃-C₁₂cycloalkyl, C₂-C₁₈alkenyl, phenyl-C₁-C₄alkyl, phenyl, naphthyl, biphenyl or a 5- or 6-membered O-, S- or N-containing heterocyclic ring, the radicals phenyl, naphthyl, biphenyl or the 5- or 6-membered O-, S- or N-containing heterocyclic ring being unsubstituted or substituted by one to five halogen, C₁-C₈alkyl, C₁-C₈alkoxy and/or C₁-C₈alkylthio;

 R_3 is C_1 - C_{18} alkyl, C_2 - C_{18} alkyl which is interrupted by one or several non-successive O atoms or which is interrupted by -CO-, -COO-, -OCO-, -CO-N(R₉)-, -N(R₉)-CO-, -N(R₉)-CO-N(R₉)-, -N(R₉)-CO-, -N(R₉)-CO-N(R₉)-, -N(R₉)-CO-R₁₀, -COO-R₁₀, -COO-R₁₀, -COO-R₁₀, -COO-R₁₀, -CO-N(R₉)-R₁₀, -C(R₁₁)=C(R₁₂)-CO-OR₁₀ or -C(R₁₁)=C(R₁₂)-phenyl;

 C_2 - C_{12} alkenyl or C_2 - C_{12} alkenyl which is interrupted by one or several non-successive O atoms; phenyl- C_1 - C_4 alkyl, phenyl, naphthyl, biphenyl, C_5 - C_{12} cycloalkyl or a 5- or 6-membered O-, S- or N-containing heterocyclic ring, the radicals phenyl, naphthyl, biphenyl, C_5 - C_{12} cycloalkyl or the 5- or 6-membered O-, S- or N-containing heterocyclic ring being unsubstituted or substituted by one to five halogen, C_1 - C_8 alkyl, C_1 - C_8 alkylthio C_1 - C_8 alkoxy and/or $-N(R_8)_2$; or R_3 is -CO- OR_9 or -CO- $N(R_9)_2$;

Q is a single bond, CR_6R_7 , -O- or -S-;

R₄ and R₅ are each independently of the other hydrogen, C₁-C₄alkyl or C₁-C₄alkoxy;

R₆ and R₇ are each independently of the other hydrogen or C₁-C₄alkyl;

 R_8 is C_1 - C_{18} alkyl, C_2 - C_{18} alkyl which is interrupted by one or several non-successive O-atoms; or - $N(R_8)_2$ forms a 5- or 6-membered O-, S- or N-containing heterocyclic ring;

 R_9 is hydrogen, C_1 - C_{18} alkyl, C_2 - C_{18} alkyl which is interrupted by one or several non-successive O atoms, C_3 - C_{12} -cycloalkyl, C_2 - C_{18} -alkenyl, phenyl- C_1 - C_4 -alkyl, phenyl, naphthyl, pyridyl, the radicals phenyl, naphthyl or pyridyl being unsubstituted or substituted by one to five C_1 - C_8 -alkyl, C_1 - C_8 -alkylthio and/or halogen; or -N(R_9)₂ forms a 5- or 6-membered O-, S- or N-containing heterocyclic ring;

 R_{10} is C_1 - C_{18} alkyl, C_2 - C_{18} alkyl which is interrupted by one or several non-successive O-atoms, C_3 - C_{12} -cycloalkyl, phenyl- C_1 - C_4 -alkyl, C_2 - C_{18} -alkenyl, phenyl, naphthyl [[,]] or biphenyl, [[;]] the radicals phenyl- C_1 - C_4 -alkyl, phenyl, naphthyl or biphenyl being unsubstituted or substituted by one to five C_1 - C_8 -alkyl, C_1 - C_8 -alkoxy, C_1 - C_8 -alkylthio and/or halogen;

 R_{11} is hydrogen or C_1 - C_4 -alkyl;

 R_{12} is hydrogen or C_1 - C_4 -alkyl;

by

(1) reacting a phosphorous halide of formula IIa or a phosphorous halide oxide of formula IIb or a phosphorous halide sulfide of formula IIc

$$R_{1} = \begin{bmatrix} \begin{bmatrix} R_{3} \end{bmatrix}_{2-m} \\ P = \begin{bmatrix} Hal \end{bmatrix}_{m} \end{bmatrix}_{n} R_{1} = \begin{bmatrix} \begin{bmatrix} R_{3} \end{bmatrix}_{2-m} \\ P = \begin{bmatrix} Hal \end{bmatrix}_{m} \end{bmatrix}_{n} R_{1} = \begin{bmatrix} \begin{bmatrix} R_{3} \end{bmatrix}_{2-m} \\ P = \begin{bmatrix} Hal \end{bmatrix}_{m} \end{bmatrix}_{n} (Ilc)$$

wherein R_1 , R_3 , n and m have the meaning cited above and Hal is F, Cl, Br or I; with an alkali metal in a solvent (**metallation**) in the presence of a proton source (**reduction**);

(2) subsequent reaction with m acid halides of formula III

wherein R₂, Hal and m have the meaning cited above.

2.(original) A process according to claim 1, wherein in step (1) the metallation is carried out by reacting a compound of the formula IIa, IIb, or IIc with an alkali metal in a solvent, whereby a metallized phosphanide of the formula V

R_1 -P(Me)-P(Me)- R_1 (V)

is formed together with cyclic phosphanes $(R_1P)_n$, $n\geq 3$ as intermediates, wherein Me is lithium, sodium or potassium or magnesium in combination with lithium, and R_1 is as defined in claim 1; and wherein the reduction is carried out by reacting the intermediate V and/or $(R_1P)_n$, $n\geq 3$ with a proton source.

3. (currently amended) A process according to claim 2, wherein the alkali metal is sodium;

the proton source is selected from the group consisting of sterically hindered alcohols, trialkylamine hydrohalogenes, bisarylamines, malono nitrile, malonic acid esters, amidine hydrohalogene and carboxylic acids;

the solvent is <u>one or more compounds selected from the group consisting of</u> benzene, toluene, o-, m- or p-xylene, mesitylene, ethylbenzene, diphenylethane, 1,2,3,4-tetrahydronaphthaline (tetraline) [[,]] <u>and</u> isopropylbenzene (cumol); <u>and mixtures thereof</u>; and

the reaction temperature of step (1) is in the range from -20°C to +160°C.

4. (currently amended) A process according to claim 3, wherein the sterically hindered alcohol is selected from the group consisting of secondary erand tertiary C₃-C₁₈alcohols._, preferably of t-butanol, tert.-amyl-alcohol, 3-methyl-3-pentanol, 3-ethyl-3-pentanol, triphenylmethanol, 3,7-dimethyl-3-octanol, 2-methyl-1-phenyl-2-propanol, 2-methyl-4-phenyl-2-butanol, fenchyl alcohol, 2,4-dimethyl-3-pentanol, 1-dimethylamino-2-propanol or hexylene glycol.

- 5. (currently amended) A process according to any one of claims 1-3, claim 1, wherein the metallation is carried out in the presence of catalytic amounts of alkali or earth alkali hydroxides or of Na, K or Li alcoholates or of alcohols.
- 6. (currently amended) A process according to any one of claims 1-3, claim 1, wherein the metallation and reduction step is carried out in the presence of an activator.
- 7. (currently amended) A process according to claim 6, wherein the activator is an amine selected from the group consisting of triethylamine, tributylamine, piperidine, morpholine, N-methylpiperidine, N-methyl morpholine er-a and polyamines. such as N,N,N',N'-tetramethylethylenediamine (TMEDA).
- 8. (currently amended) A process according to claim 1 for the preparation of monoacylphosphanes of the formula I'

(1) reacting organic phosphorus halides of formula II'

 R_1 -P(Hal)₂ (II')

with an alkali metal in a solvent in the presence of a proton source; and either

(2a) subsequent reaction with an acid halide of formula III'

Hal
$$\stackrel{\mathsf{O}}{=} \mathsf{R}_2$$
 (III')

followed by the reaction with an electrophilic compound R_3 -Hal, or-vice-versa,

(2b) subsequent reaction with with an electrophilic compound R₃-Hal followed by the reaction with an acid halide of formula III'

wherein R₁, R₂ and R₃ and Hal are as defined in claim 1.

9. **(currently amended)** A process according to claim 1 for the preparation of **symmetric bisacylphosphanes** of the formula I'' (compounds of the formula I with n=1 and m=2)

$$R_{2}$$
 C P C R_{2} R_{1} $(I"), by$

(1) reacting organic phosphorus halides of formula II" R_1 -P(Hal)₂ (II")

with an alkali metal in a solvent in the presence of a proton source;

(2) subsequent reaction with an acid halide of formula III"

wherein R₁ and R₂ and Hal are as defined in claim 1.

10. **(original)** A process according to claim 1 for the preparation of **unsymmetric bisacylphosphanes** of the formula I'''

$$R_{2}'$$
 C P C R_{2} R_{1} (I''') by

(1) reacting organic phosphorus halides of formula II" R₁-P(Hal)₂ (II")

with an alkali metal in a solvent in the presence of a proton source;

(2) subsequent reaction with an acid halide of formula III"

$$\mathsf{Hal} \overset{\mathsf{O}}{-\!\!\!\perp\!\!\!\perp} \mathsf{R_2} \quad \mathsf{(III")}$$

(3) subsequent reaction with a second acid halide III""

wherein

R₁ is as defined in claim 1 and

 R_2 and R_2 ' independently of one another are as defined in claim 1 under R_2 with the proviso that R_2 is not equal R_2 ',

Hal is as defined in claim 1.

- 11. **(original)** A process according to claim 1, wherein step (1) is carried out by reacting diphospanes of the formula $(R_1)_2$ -P-P(R_1)₂ or polyphosphanes of the formula $[R_1$ P]n, wherein R_1 is as defined above and n is \geq 3, with an alkali metal in a solvent in the presence of a proton source; followed by the reaction with acid halides (III, III', III'') and/or by reaction with electrophilic compounds R_3 -Hal.
- 12. **(currently amended)** A process <u>according to claim 1</u> for the preparation of mono acylated phosphanes of the formula VI and VI'

(1) reacting organic phosphorus halides of formula II" R_1 -P(HaI)₂ (II")

with an alkali metal in a solvent in the presence of a proton source;

(2) subsequent reaction with an acid halide of formula III" or III"

Hal
$$\stackrel{O}{\longrightarrow} R_2$$
 (III")

wherein R_1 , R_2 are as defined in claim 1, R_2 ' is as defined in claim [[10]] 1 under R_2 with the proviso that R_2 is not equal R_2 ' and Me is Li, Na, K or Mg in combination with Li.

~93

1.90

1.13

13. (currently amended) A process according to claim 1, further comprising an additional step of oxiding or reacting the acylphosphane of formula (I) with sulfur for the preparation of to prepare acylphosphane oxides and acylphosphane sulfides of formula IV

(IV), wherein

R₁, R₂, R₃, n and m are as defined in claim1, and Z is O or S_.—, by oxidation or reaction with sulfur of the acylphosphane of formula I, I', I'' or I''' as defined in claims 1,8,9 and 10.

- 14. **(new)** A process according to claim 4, wherein the secondary and tertiary C₃-C₁₈alcohols are selected from the group consisting of t-butanol, t-amyl-alcohol, 3-methyl-3-pentanol, 3-ethyl-3-pentanol, triphenylmethanol, 3,7-dimethyl-3-octanol, 2-methyl-1-phenyl-2-propanol, 2-methyl-4-phenyl-2-butanol, fenchyl alcohol, 2,4-dimethyl-3-pentanol, 1-dimethylamino-2-propanol or hexylene glycol.
- 15. **(new)** A process according to claim 5, wherein metallation is carried out in the presence of catalytic amounts of Na, K or Li sterically hindered alcoholates or sterically hindered alcohols.
- 16. **(new)** A process according to claim 7, wherein the polyamine is N,N,N',N'-tetramethylethylenediamine.
- 17. (new) A process according to claim 13, wherein a monoacylphosphane of formula I'

$$R_1 - P - C - R_2$$
 (I'), is oxidized or reacted sulfur.

18. (new) A process according to claim 13, wherein a symmetric bisacylphosphane of formula I"

(I"), is oxidized or reacted sulfur.

19. (new) A process according to claim 13, wherein an unsymmetric bisacylphosphane of formula I"

(I"")), is oxidized or reacted sulfur.